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By

S. H. Carr

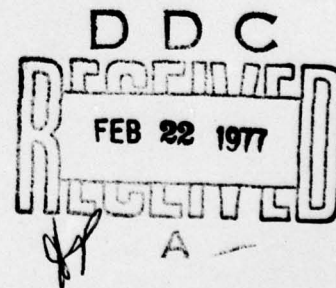
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) This paper is a preliminary, abridged review of current ideas regarding mobile ionic species in polymer electrets. The chief concept is that much of the persistent electrical polarization, developed in polymers prepared for piezo- or pyroelectric applications, is due to displaced ions. It is recognized that 1) preferential orientation of dipolar parts of the macromolecules (e.g., side groups) and 2) fluctuations in supermolecular order (including crystalline regions) lead to inhomogenieties in internal electrical fields which affect where such mobile ions become stabilized		

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(trapped). Emphasis is placed on results obtained recently from research on polyacrylonitrile electrets.

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"ROLE OF MOBILE IONIC SPECIES IN POLYMER ELECTRETS"

POLYMER ELECTRETS

An exciting new category of polymer solids, polymer electrets, has been the subject of intense research and development activities during the past eight, or so, years (1-3). The primary properties possessed by these materials are piezoelectricity and pyroelectricity, and the kinds of devices that can exploit these properties include microphones and heat detectors. Polymer electrets also can serve as radiation dosimeters or imaging devices (4). In addition, devices which can exploit the ferroelectric behavior of certain polymer electrets can be designed to store information which is in the form of electrical signals. Some of the polymers used in these applications are commonly available solids, such as polyvinylchloride, polymethylmethacrylate, and especially polyvinylidene fluoride (PVF_2). Other polymer electrets contain fillers which themselves may be piezoelectric materials. However, in all cases, it is common for the polymer to have been subjected to a thermoelectric treatment which imparts a persistent electrical polarization to the solid. Some of these materials may actually exhibit a spontaneous polarization behavior, but it is usually regarded as necessary for the sake of reproducibility that the polarization process must be applied to each of these kinds of solids in order to get the appropriate performance desired.

This persistent electrical polarization arises from a combination of individual effects (5-7). One such contribution to this polarization is preferential orientation of groups of atoms having permanent dipole moments. This polarization requires, of course, that the macromolecules in question actually possess dipolar moieties, but even in the case of polyethylene there is the possibility that the very dilute concentration of carbonyl groups can contribute some degree of persistent electrical polarization. The other kind of polarization arises from the asymmetric displacement of ionic species. This can be achieved either by permitting ions already present in the solids to be rearranged during the electrical polarization process, or they can be injected from the surroundings during polarization (8-14). Both origins of a persistent electrical polarization give rise to what is called a heterocharge, because the surfaces of the dielectric have a polarity in opposition to that of the polarizing electrode adjacent to that surface.

Persistent electrical polarization due to preferential orientation of dipoles is known to give predictable levels of piezo- and pyroelectricity (2). Although this work by Broadhurst, et al. (1,2) has rather successfully characterized the case for noncrystalline polymers, the situation with the semicrystalline polymers has been a bit more complicated (15). For example, in the case of PVF_2 (see ref. 2), it is absolutely necessary to utilize copolymers in which the phase II crystal polymorph is

avored. In both nylons (15) and PVF_2 , the crystal polymorph necessarily must have a permanent dipole moment to each unit cell in order for there to be appreciable piezoelectricity demonstrated by their respective solid. Stretching PVF_2 (16,17) has been shown to be an effective way to vary piezoelectric activity. Likewise, stretching polyacrylonitrile (PAN) leads to improvements in electrical polarization by factors ranging from 3 to 10 (18).

Homocharges, i.e. surface charge whose sign is the same as that of the polarizing electrode next to it, can be induced in a number of ways, one important one of which is by exposure to a corona discharge (19-25). Analysis of electrets made by the corona discharge technique has revealed several interesting features of such solids. The first is that the homocharges are trapped in the solids at different energy levels. The second is that the heterocharge, to whatever extent it exists, interacts with the homocharge, with the possibility of cancelling the overall polarization. Often when the physical microstructure of the solid, e.g. polyethylene terephthalate, is taken into account, one notices that heterocharge and homocharge can actually stabilize each other at the surface layers. Another way to create homocharges is by direct ion injection from the surfaces (25). In this work by Osaki and Ishida (25), it is seen that it is possible to put Na, Ca, Al, and Cl into PVF_2 films. The resulting nonuniform charge distribution can be analyzed to get information on the diffusion of such ionic impurities under the influence of electrical fields. Of course, polyelectrolytes also can act as strong electrets (26-29). Here, variation of the composition of the solid (as for example the formation of polymer blends) or the degree of saponification of polyelectrolytes will produce very different kinds of electret properties. It is likely that there is further exploitation of this line of polymers that needs to be pursued. Finally, the direct injection of electrons from the surroundings has also been investigated for its ability to make polymer electrets (29-32). Perhaps the most effective way to achieve a persistent electrical polarization for most of the technical applications exploited so far is the corona discharge in combination with direct electron injection. Certainly the extent to which any chemical reaction can occur at surfaces being exposed to incoming ionizing particles will determine the effect that results and the piezoelectric or pyroelectric activity that is achieved.

PERSISTENT ELECTRICAL POLARIZATION IN PAN

As inferred from the thermally stimulated discharge current analysis of PAN electrets (18,33-36), this polymer can achieve very high levels of persistent electrical polarization. However, unpublished results from experiments measuring the piezo-

and pyroelectric properties of polarized PAN have revealed only a modest level of performance. This puzzle is just now being unraveled, and it appears that much of the charge stored in PAN is in the form of a monopole (2) electret. There is clear evidence from birefringence measurements, infrared dichroism studies, and x-ray diffraction analysis that a preferred orientation of the nitrile side groups does exist in these films. In fact, even films which have never been subjected to the thermoelectric polarizing treatment exhibit substantial levels of persistent electrical polarization themselves. This kind of spontaneous polarization behavior is unusual but has been attributed to what takes place during the casting of films of dimethyl formamide (DMF) solutions.

Figure 1 gives a thermally stimulated discharge (TSD) spectrum (5) revealing three temperature ranges over which there are discharge current maxima. The one above 90°C, labeled γ , has been attributed (18,34-36) to the randomization of nitrile side groups which have adopted a preferred orientation. The peak labeled β , which occurs in the temperature range of 140 to 160°C, appears (Fig. 2) to be due to the onset of mobility for sorbed ionic species. The peak at the temperature range 180 to 205°C, labeled the α peak, has recently been attributed to the earliest stages of thermodegradation of PAN (36). The final current seen in the temperature range above 215°C appears to represent wholesale degradation of this polymer. The importance of this study is that it provides some understanding of the various contributions to polarization in PAN, and it is clear that a variety of phenomena are operating at the same time. One notes from Fig. 1 that the γ peak is of polarity opposite to that of the α and β peaks; this is seen only in the case of unpolarized PAN films. What is thought to be occurring here is that during the process by which solvent evaporates through the top surface of a PAN film, the ionic impurities become redistributed and create such an internal electrical field that the nitrile side groups adopt a preferential orientation in opposition to this ion-induced electrical asymmetry.

When an electrical field is applied to the PAN films at elevated temperatures, several things happen at once. Firstly, the polymer undergoes a molecular reorganization which leads to the creation of inherent crystalline domains (18). Secondly, the nitrile side groups undergo a reorientation in response to the externally applied field and therefore have a polarization which is the same sign as that of the ions which depolarize in the temperature range of the β peak. In some cases, the γ peak is actually reduced in intensity on polarized films from what is observed with unpolarized films. This is thought to be due to the masking of the external field by the internally sorbed impurity ions. The α peak also responds to the imposition of an external electric field, but the reason for this is not

quite so clear. It is currently advanced (36) that DMF molecules residual in these films also undergo some diffusion under the influence of an externally applied field, and therefore become asymmetrically distributed, just as the other sorbed ions do. It has been observed from this study that DMF molecules actually accelerate the thermal degradation of PAN, and so one would expect the side of a film to which the DMF had diffused as being the side on which the initial stages of thermal degradation (and attending production of ions) occurs. Figure 2 supports some of these assertions. It can be seen that when nitrate ions are doped (38) in PAN films, the enhancement of concentration (as seen by ATR infrared absorption spectroscopy) reveals the onset of mobility at the upper range of the β peak. Likewise, enhanced residual DMF concentration is seen to decay over the same temperature as the β peak. Diffusion of such small molecular or ionic species is controlled largely by the onset of segmental mobility in such disordered polymers, and so one infers that the kind of chain mobility required for these redistributions is available only in these higher temperature ranges. One would similarly infer that the γ peak corresponds to the onset of motions that relate only to the environment of nitrile groups themselves and not of the chains to which they are attached.

In summary for polarized PAN, one can see in Figure 3 a schematic representation of a film seen in cross section. The elliptical domains are intended to be ordered regions in which a permanent dipole is created by virtue of an asymmetric placement of the nitrile groups (18), and surrounding these domains are ionic species which give rise to a kind of Maxwell-Wagner (39,40) polarization. Depending upon the relative concentrations of negative and positive ions, there may be a complete masking of polarizations contributed by these domains; in addition, if negative ions are more abundant on one surface than the other (or conversely with positive ions), then there can be a persistent polarization that is present in these films even though they are unpolarized. When such films are stretched uniaxially, it is assumed that the ordered regions will adopt some sort of order coherence with regard to their neighboring domains. It would be imagined furthermore that counterions would reorganize such that they preserve the Maxwell-Wagner polarizations that they created earlier. Such stretched, but as yet unpolarized, films still would lack any polarization other than that which occurred during the initial formation of the films. However, if these films are subsequently subjected to a polarizing thermoelectric treatment, then it is imagined that nitrile groups within these ordered regions will undergo a slight rearrangement permitting the resulting dipole moments of these domains to align in a single direction. Diffusion of the counterions can begin to occur at the same time, with the

result that some of the shielding of the polarization arising from these domains is now lost, and at the same time buildup of some charged species can begin to occur in the region of the surfaces against electrodes of the opposite polarity. Diffusion of the species is expected to be impeded by the presence of these ordered domains, as they should have higher masked density than the surrounding matrix. One may speculate, in view of all of this, that the electrical polarization possible in such polymers as polyacrylonitrile might be enhanced further by the deliberate incorporation of ionic species such as those found in polyacrylonitrile.

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FIGURE CAPTIONS

Fig. 1. Thermally stimulated discharge (TSD) current spectrum for PAN that had never been subjected to a thermoelectric polarizing treatment. Data from ref. 35.

Fig. 2. TSD from polarized PAN, along with data for corresponding surface concentrations of residual DMF or doped nitrate.

Fig. 3. Schematic representation of internal electrostatic non-uniformities in PAN.

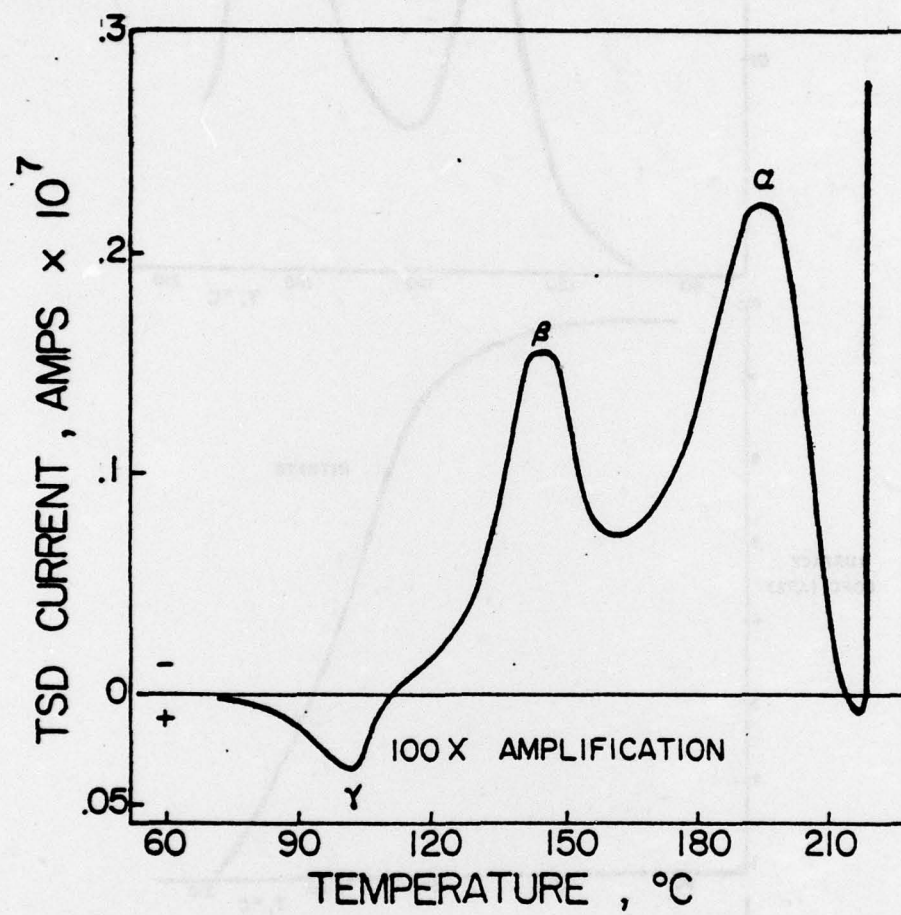


Fig. 1

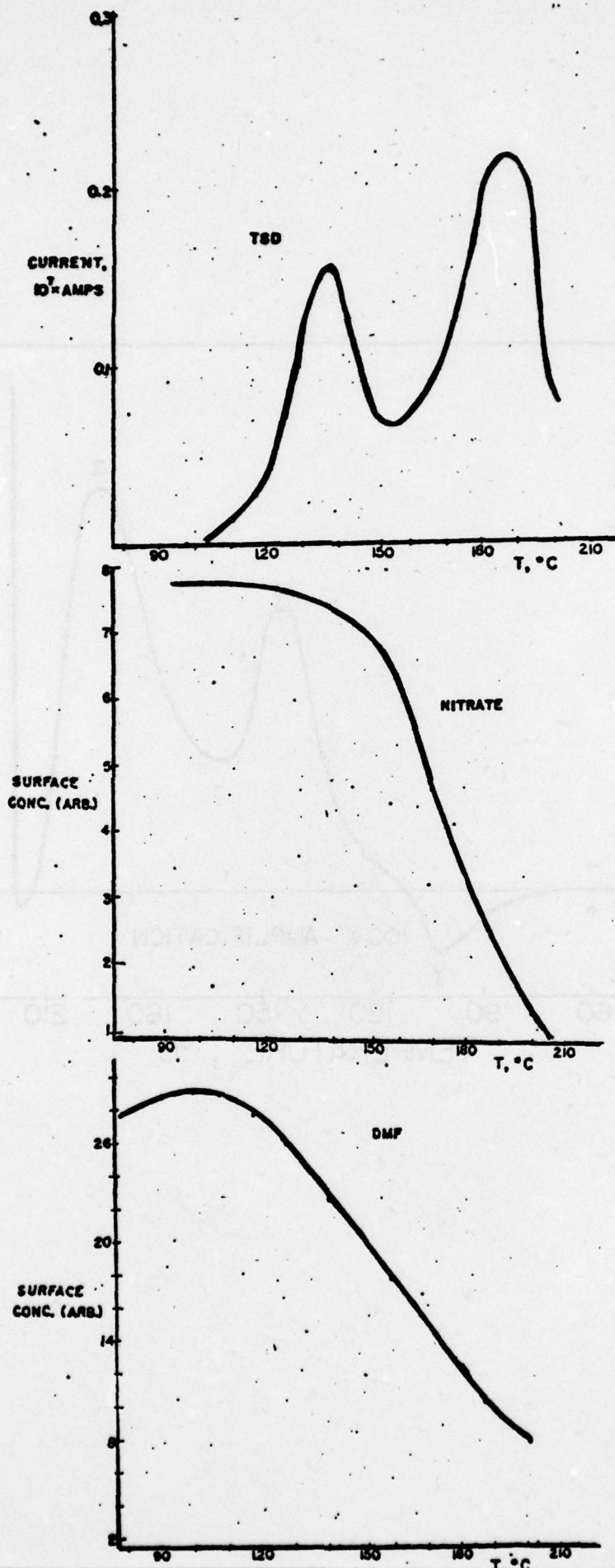
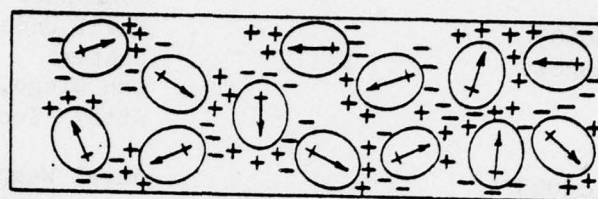
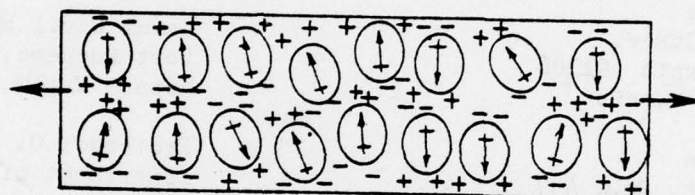


Fig. 2

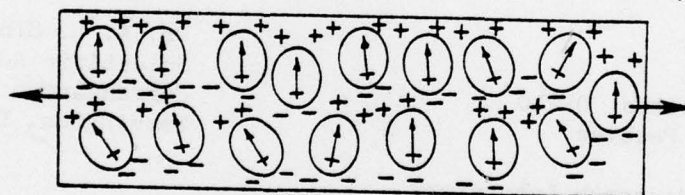
INHOMOGENIETIES IN PAN



annealed



stretched



stretched-polarized

Fig. 3

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